

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 582 355 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
22.05.1996 Bulletin 1996/21

(51) Int Cl.<sup>6</sup>: **C08F 210/02, C08F 232/08**(21) Application number: **93202803.8**(22) Date of filing: **01.02.1985**(54) **Random copolymer**

Statistische Copolymere

Copolymères statistiques

(84) Designated Contracting States:  
DE FR GB IT NL

(30) Priority: 03.02.1984 JP 16995/84  
12.11.1984 JP 236828/84

(43) Date of publication of application:  
09.02.1994 Bulletin 1994/06

(62) Application number of earlier application in  
accordance with Art. 76 EPC: 85300706.0

(73) Proprietor: MITSUI PETROCHEMICAL  
INDUSTRIES, LTD.  
Tokyo 100 (JP)

(72) Inventors:  
• Kajitara, Hirokazu, c/o Mitsui Petrochem. Ind. Ltd.  
Yamaguchi 740 (JP)  
• Oda, Hidekuni,  
C/O Chiba Works of Mitsui Petroch.  
Chiba 299-01 (JP)

• Minami, Syuji, c/o Mitsui Petrochemical Ind. Ltd.  
Yamaguchi 740 (JP)

(74) Representative: Crosswell, Thomas Anthony et al  
J.A. KEMP & CO.  
14 South Square  
Gray's Inn  
London WC1R 5LX (GB)

(56) References cited:  
FR-A- 1 535 460 FR-A- 2 276 320  
LU-A- 67 835

• PATENT ABSTRACTS OF JAPAN no. 994  
(C-78)(14) & JP-A-53 034 890 (NIPPON GOSEI  
GOMU K. K.) 31 March 1978  
• PATENT ABSTRACTS OF JAPAN no. 994  
(C-78)(14) & JP-A-53 034 890

Remarks:

The file contains technical information submitted  
after the application was filed and not included in this  
specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## EP 0 582 355 B1

## Description

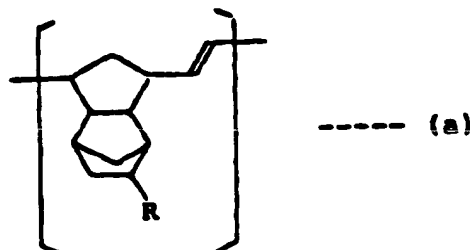
This invention relates to a random copolymer comprising at least ethylene and a 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene as monomers. More specifically, it relates to a copolymer having excellent transparency and a well balanced combination of heat resistance, heat aging resistance, chemical and solvent resistance, dielectric properties and mechanical properties such as rigidity. This application is divided from application no. 85 300 706.0.

Polycarbonate, poly(methyl methacrylate) and poly(ethylene terephthalate) are known as synthetic resins having excellent transparency. The polycarbonate resin has excellent heat resistance, heat aging resistance and impact strength as well as excellent transparency, but have the defect of poor chemical resistance whereby it is readily attacked by strong alkalis. Poly(methyl methacrylate) has the defect that it is susceptible to attack by ethyl acetate, acetone and toluene, is swollen in ether, and has low heat resistance. Polyethylene terephthalate has excellent heat resistance and mechanical properties but has the defect of possessing weak resistance to strong acids or alkalis and being susceptible to hydrolysis.

Many of polyolefins well known as general-purpose resins have excellent chemical resistance, solvent resistance and mechanical properties, but have poor heat resistance. Furthermore, they have poor transparency because they are crystalline. The transparency of polyolefins is generally improved by adding a nucleating agent to render the crystal structure fine, or by performing quenching to stop the growth of crystals, but such measures have not proved to be entirely effective. Rather, the addition of a third component such as the nucleating agent is likely to impair the inherent excellent properties of the polyolefins. Furthermore, the quenching method requires large scale equipment, and is also likely to reduce heat resistance or rigidity with a decrease in crystallinity.

On the other hand, methods have been proposed for producing polymers having superior transparency by copolymerizing ethylene with bulky comonomers. U. S. Patent 2,883,372 discloses a copolymer of ethylene with 2,3-dihydrodicyclopentadiene. This copolymer has a well balanced combination of rigidity and transparency but low heat resistance as shown by its glass transition temperature of about 100°C.

Japanese Patent Publication No. 14,910/1971 discloses a process for producing a homo- or co-polymer having polymerized units represented by the following formula (a)



wherein R is hydrogen or a lower alkyl group, which comprises polymerizing a 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the following formula (b)



wherein R is as defined above, alone or with a cyclic olefin selected from styrene, acenaphthylene, bicyclo-[2.2.1]heptene-2, alkyl-substituted products of the heptene and cyclopentene in the presence of an alcohol as a reducing agent using a halide of a noble metal such as ruthenium as a catalyst.

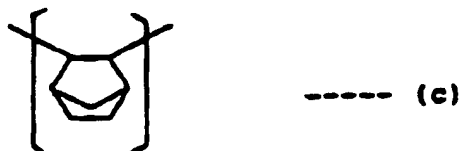
Homo- or co-polymers comprising the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene as a part or the whole of monomers and methods for production thereof are also disclosed in Japanese Laid-Open Patent Publications Nos. 159,598/1975, 127,728/1983, 51,911/1984, 81,315/1984 and 81,316/1984 and U. S. Patent 4,178,424.

The polymers disclosed in these prior art documents are ring-opened polymers having polymerized units resulting from ring-opening of monomers as in the polymerized units represented by formula (a). As can be understood from the formula (a), these ring-opened polymers are structurally characterized by the fact that the main polymer chain contains an unsaturated vinyl linkage. Because of the presence of the unsaturated vinyl linkage, these polymers have poor heat aging resistance.

All of the polymers described in the above prior art documents are ring-opened polymers obtained by the ring scission of monomer. U. S. Patents 3,330,815 and 3,494,897 and Journal of Polymer Science: Polymer Physics Edition, volume 12, 1607-1618 (1974) describe polymers of the type obtained by the opening of the double bond of monomer without the ring scission of the bicyclohept-2-ene skeleton of the monomer.

## EP 0 582 355 B1

U. S. Patent 3,330,815 discloses that a polymer comprising polymerized units of the following formula (c)



or the substitution product thereof is obtained from bicyclo[2.2.1]hept-2-ene of the following formula (d)



or its substitution product.

U. S. Patent 3,494,897 discloses a process for producing a copolymer of ethylene with a bicyclo[2.2.1]hept-2-ene represented by the following formula (e)



Example 44 and claim 92 of this patent discloses a copolymer of ethylene with tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]-4-dodecene of the following formula (f) encompassed within the formula (e)



and ethylene. The Patent does not describe the content of the tetracyclododecene of the copolymer of Example 44. When it is calculated under the assumption that all of the tetracyclododecene charged was introduced into the polymer, the polymer contains polymerized units derived from about 2 mole% at most of the tetracyclododecene. U. S. Patent 3,494,897 does not at all describe specifically copolymers of ethylene with tetracyclododecenes other than the tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]-4-dodecene of formula (f).

Journal of Polymer Science: Polymer Physics Edition, volume 12, 1607-1618 (1974) discloses copolymers of ethylene and norbornene derivatives having dynamic mechanical properties. Table II of this document shows a copolymer of ethylene containing 1 mole% of polymerized units derived from the same compound as formula (f) (named octahydrodimethanonaphthalene in this document). Table IV thereof states that this copolymer has a beta-relaxation temperature of 15°C.

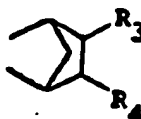
The copolymers described in these prior art references which contain only 2% at the largest of octahydrodimethanonaphthalene have a glass transition temperature of about 15°C at the highest. They strongly exhibit a rubbery nature and have poor heat resistance and mechanical properties.

The present invention provides a transparent random copolymer characterized in that

(A) said copolymer comprises polymerized units derived from ethylene and polymerized units derived from 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the following formula (1)



wherein R<sub>1</sub> and R<sub>2</sub> are identical or different and each represents a hydrogen atom, a halogen atom or an alkyl group, or R<sub>1</sub> and R<sub>2</sub> may be bonded to each other to form a trimethylene group or a group represented by the following formula



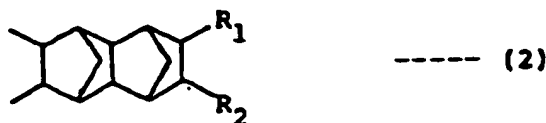
in which R<sub>3</sub> and R<sub>4</sub> are identical or different and each represents a hydrogen atom, a halogen atom or an

## EP 0 582 355 B1

alkyl group,

(B) the mole ratio of polymerized units derived from 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to polymerized units derived from ethylene is from 3:97 to 95:5,

(c) the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is incorporated in the polymer chain as polymerized units represented by the following formula (2)



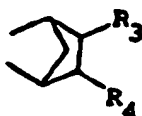
wherein  $R_1$  and  $R_2$  are as defined above, and

(D) said copolymer has a glass transition temperature, measured by a dynamic mechanical analyzer, of at least 25°C, subject to the proviso that said copolymer does not consist essentially of said at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the formula (1), ethylene and at least one alpha-olefin of at least 3 carbon atoms and/or cycloolefin, wherein the mole ratio of polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to polymerized units from ethylene is from 3:97 to 95:5, and the mole ratio of polymerized units from the at least one alpha-olefin and/or cycloolefin to the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is from 95:5 to 20:80.

The present invention also provides a process for producing a transparent random copolymer as defined above which comprises copolymerizing a monomer mixture comprising ethylene and at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of the formula (1) in a hydrocarbon medium under a pressure of up to 4.9 MPa (0 to 50 kg/cm<sup>2</sup>) in the presence of a catalyst formed from a vanadium compound and an organoaluminum compound which are soluble in the hydrocarbon medium.

The present invention further provides shaped articles of a transparent random copolymer as defined above.

The 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, i.e. a tetracyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>]-4-dodecene, used in this invention is represented by the above formula (1). In formula (1),  $R_1$  and  $R_2$  are identical or different and each represents a hydrogen atom, a halogen atom or an alkyl group, or  $R_1$  and  $R_2$  are bonded to each other to form a trimethylene group or a group of the following formula



wherein  $R_3$  and  $R_4$  are identical or different and each represents a hydrogen atom, a halogen atom or an alkyl group.

Examples of the halogen atom for  $R_1$  to  $R_4$  are fluorine, chlorine and bromine. The alkyl group for  $R_1$  to  $R_4$  may be linear or branched, and preferably has 1 to 20 carbon atoms, particularly 1 to 10 carbon atoms. Examples of the alkyl group include methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl.

Examples of the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of formula (1) include

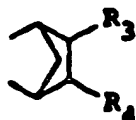
- 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-propyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-stearyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-decyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2,3-dimethyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-cyclohexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-isobutyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,

## EP 0 582 355 B1

2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 12-ethyl-hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]heptadecene-4,  
 12-methyl-hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]heptadecene-4,  
 12-isobutyl-hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]heptadecene-4,  
 hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]heptadecene-4, and  
 pentacyclo[6,5,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,13</sup>]pentadecene-4.

These 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalenes may be used singly or in combination.

Among the compounds of formula (1), those in which at least one of  $R_1$  and  $R_2$  is an alkyl group, especially having 1 to 10 carbon atoms, above all 1 to 5 carbon atoms, or  $R_1$  and  $R_2$  are bonded together to form a trimethylene group or a group of the formula



wherein  $R_3$  and  $R_4$  are as defined above, and preferably represent an alkyl group having an alkyl group with 1 to 10 carbon atoms, especially 1 to 5 carbon atoms, are preferred.

The compound of formula (1) can be produced, for example, by subjecting the corresponding norbornene and cyclopentadiene to the Diels-Alder reaction.

According to the process of this invention, the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of formula (1) is copolymerized with ethylene in a hydrocarbon solvent in the presence of a catalyst.

The catalyst used is one formed from a vanadium compound and an organoaluminum compound which are soluble in the hydrocarbon solvent used.

Suitable vanadium compounds include vanadium halides such as  $VCl_4$ ,  $VBr_4$ ,  $VCl_3$  and  $VBr_3$ ; vanadium oxyhalides such as  $VOCl_3$ ,  $VOBr_3$ ,  $VOCl_2$  and  $VOBr_2$ ; and vanadium compounds of the formula  $VO(OR)_nX_{3-n}$  wherein R represents a hydrocarbon group, X represents a halogen atom, and n is a number represented by  $0 < n \leq 3$ . Of these, hydrocarbon-soluble vanadium compounds, particularly the vanadium oxyhalides and the compounds of the formula  $VO(OR)_nX_{3-n}$  are preferred. In the compounds of the formula  $VO(OR)_nX_{3-n}$ , R is an aliphatic, alicyclic or aromatic hydrocarbon group, preferably an aliphatic hydrocarbon group with 1 to 20, preferably 1 to 5, especially preferably 1 to 3, carbon atoms. The number n is  $0 < n \leq 3$ , preferably  $1 \leq n \leq 1.5$ . Specific examples of these vanadium compounds are  $VO(OCH_3)Cl_2$ ,  $VO(OCH_3)_2Cl$ ,  $VO(OCH_3)_3$ ,  $VO(OC_2H_5)Cl_2$ ,  $VO(OC_2H_5)_2Cl$ ,  $VO(OC_2H_5)_3$ ,  $VO(OC_2H_5)_2Br$ ,  $VO(OC_2H_5)Br_2$ ,  $VO(OC_3H_7)Cl_2$ ,  $VO(OC_3H_7)_2Cl$ ,  $VO(OC_3H_7)_3$ ,  $VO(O-n-C_4H_9)Cl_2$ ,  $VO(O-n-C_4H_9)_2Cl$ ,  $VO(O-iso-C_4H_9)Cl_2$ ,  $VO(O-sec-C_4H_9)_2Cl$ , and  $VO(OC_6H_{11})_2Cl$ . Mixtures of these may also be used. These vanadium compounds can easily be obtained by, for example, reacting  $VOCl_3$  with alcohols, or  $VOCl_3$  with  $VO(OR)_3$ .

Suitable organoaluminum compounds used together with the vanadium compounds are compounds represented by the general formula  $R'_mAlX'_{3-m}$  wherein R' represents a hydrocarbon group, preferably an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 20 carbon atoms, especially 1 to 10 carbon atoms, X' represents a halogen atom, especially fluorine, chlorine or bromine, and m is a number represented by  $0 < m \leq 3$ . Halogen-containing organoaluminum compounds of the above formula in which m has an average value represented by  $1 \leq m \leq 2$ , particularly  $1.2 \leq m \leq 1.8$ , are preferred. Specific examples of these organoaluminum compounds are trialkyl aluminums such as triethyl aluminum, triisopropyl aluminum, triisobutyl aluminum, tri(n-propyl) aluminum and tri(n-butyl) aluminum; dialkyl aluminum monohalides such as diethyl aluminum monochloride, diethyl aluminum monobromide, diisopropyl aluminum monochloride, diisopropyl aluminum monobromide, di(n-propyl) aluminum monochloride, di(isobutyl) aluminum monochloride, di(n-butyl) aluminum monochloride, di(sec-butyl) aluminum monochloride, di(n-pentyl) aluminum monochloride and dioctyl aluminum monochloride; alkyl aluminum sesquihalides such as ethyl aluminum sesquichloride, isopropyl aluminum sesquichloride, n-propyl aluminum sesquichloride, n-butyl aluminum sesquichloride, n-pentyl aluminum sesquichloride and n-octyl aluminum sesquichloride; and alkyl aluminum dihalides such as ethyl aluminum dichloride, ethyl aluminum dibromide, isopropyl aluminum dichloride, isopropyl aluminum dibromide, n-propyl aluminum dichloride, n-propyl aluminum dibromide, n-butyl aluminum dichloride, isobutyl aluminum dichloride, sec-butyl aluminum dichloride, n-pentyl aluminum dichloride and n-octyl aluminum dichloride. Mixtures of these may also be used.

The ratio of the organoaluminum compound to the vanadium compound, in terms of the mole ratio of Al to V, is at least 1, preferably not more than 30, especially preferably from 2 to 20.

The copolymerization is carried out in a hydrocarbon solvent. Examples of the solvent include aliphatic hydrocarbons having 5 to 15 carbon atoms such as pentane, hexane, heptane, octane and kerosene; alicyclic hydrocarbons having 5 to 15 carbon atoms such as cyclopentane and cyclohexane; and aromatic hydrocarbons having 6 to 15 carbon

## EP 0 582 355 B1

atoms such as benzene, toluene and xylene. These solvents may be used singly or in combination.

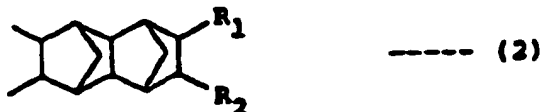
Preferably, the copolymerization is carried out such that the concentration of the vanadium compound in the reaction medium is from 0.05 to 20 millimoles/liter, preferably 0.1 to 10 millimoles/liter. The organoaluminum compounds is used in such a concentration that the Al/V mole ratio becomes at least 1, preferably not more than 30, especially preferably from 2 to 20.

The ratio of ethylene to the compound of formula (1) varies according to the composition of the desired copolymer, the type of the reaction medium, the polymerization temperature, etc. Generally, the mole ratio of ethylene to the compound of formula (1) is adjusted to 100:1 to 1:100, preferably 50:1 to 1:50.

The polymerization temperature is from -50 to 100°C, preferably from 30 to 80°C. The polymerization pressure is maintained at 0 to 4.9 MPa (0 to 50 kg/cm<sup>2</sup>), preferably at 0 to 1.0 MPa (0 to 20 kg/cm<sup>2</sup>). The molecular weight of the polymer may be controlled by using a molecular controlling agent such as hydrogen as required.

As a result, the process of this invention gives the random copolymer of this invention in which the mole ratio of polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of formula (1) to polymerized units from ethylene (measured by <sup>13</sup>C-NMR analysis) is in the range of from 3:97 to 95:5. Preferably, the above mole ratio is from 5:95 to 80:20, more preferably from 10:90 to 80:20.

The compound of formula (1) is incorporated into the chain of the random copolymer of the invention as polymerized units of the following formula (2)



wherein R<sub>1</sub> and R<sub>2</sub> are as defined hereinabove. The random copolymers of the invention, therefore, have an iodine number of usually not more than 5, and most of them have an iodine number of not more than 2. The random copolymers of this invention have an intrinsic viscosity  $[\eta]$ , measured in decalin at 135°C, of preferably 0.005 to 20 dl/g, more preferably 0.01 to 15 dl/g, especially preferably 0.05 to 10 dl/g.

The novel random copolymers of this invention are generally amorphous or of low crystallinity. Preferably, they are amorphous. Accordingly, they have good transparency. Generally, these copolymers have a crystallinity, determined by X-ray diffraction, of not more than 40%, preferably not more than 25%.

The copolymer of the invention has a melting point, determined by a differential scanning calorimeter (DSC), of not more than 135°C, preferably not more than 128°C.

The superior heat resistance of the novel random copolymer of this invention can also be substantiated by its high glass transition temperature. Specifically, the novel random copolymer of the invention has a glass transition temperature (T<sub>g</sub>), measured by a dynamic mechanical analyzer, of at least 25°C, preferably 30 to 220°C, more preferably 80 to 200°C.

The random copolymer of this invention has a density, determined by the density gradient tube method in accordance with ASTM D1505, of usually at least about 0.86 g/cm<sup>3</sup>, preferably 0.94 to 1.30 g/cm<sup>3</sup>, especially preferably 0.96 to 1.10 g/cm<sup>3</sup>.

The random copolymer of this invention also has excellent electrical properties, and for example, has a dielectric constant, measured at 1 KHz, of 1.5 to 4.0, above all 1.7 to 2.6.

Novel random copolymers of this invention in which the mole ratio of the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to the polymerized units from ethylene is from 10:90 to 90:10, preferably from 15:85 to 80:20 (measured by <sup>13</sup>C-NMR analysis), and which have an intrinsic viscosity, measured in decalin at 135°C, of 0.3 to 15 dl/g, preferably 0.5 to 10 dl/g, a crystallinity, determined by X-ray diffraction, of not more than 25%, preferably not more than 10%, and a melting point, measured by a differential scanning calorimeter, of not more than 128°C, preferably not more than 100°C, and a glass transition temperature measured by a dynamic mechanical analyzer (DMA) made by Du Pont of at least 80°C, preferably 100 to 220°C, have excellent transparency, processability, heat resistance, heat aging resistance, chemical and solvent resistance, dielectric properties and mechanical properties such as rigidity. Accordingly, these copolymers can be used as a transparent resin in various fields including an optical field as optical lenses, optical disks, optical fibers and window-panes, an electrical field as water tanks for electric irons, articles used for electronic ovens, substrates for liquid crystal display, substrates for printed circuit boards, substrates for high frequency circuits, and transparent electrically conductive sheets or films, medical and chemical fields as injection syringes, pipettes and animal gauges, and in other fields as camera bodies, housings of various measuring instruments, films, sheets and helmets.

Novel random copolymers of this invention in which the mole ratio of the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to the polymerized units from ethylene is from 10:90 to 90:10, preferably from 15:85 to 80:20 (measured by <sup>13</sup>C-NMR analysis), and which have an intrinsic viscosity, measured in decalin at

## EP 0 582 355 B1

135°C, of 0.005 to 0.3 dV/g, preferably 0.01 to 0.3 dV/g, especially preferably 0.05 to 0.2 dV/g, a crystallinity, determined by X-ray diffraction, of not more than 25%, preferably not more than 10%, a melting point, measured by a differential scanning calorimeter, of not more than 128°C, preferably not more than 100°C, a glass transition temperature measured by a dynamic mechanical analyzer (DMA) made by Du Pont of at least 80°C, preferably 100 to 220°C, and a viscosity at 280°C of 100 to  $2 \times 10^6$  centipoises, preferably 100 to  $2 \times 10^4$  centipoises are of relatively low molecular weight and have excellent transparency, heat resistance, heat aging resistance, dielectric properties and chemical and solvent resistance. Hence, they are useful as synthetic waxes in various applications. For example, these low-molecular-weight random copolymers of the invention can find extensive use as candles, impregnating agents for matchwood, paper processing agents, sizing agents, rubber antioxidants, waterproofing agents for cardboards, retarders for chemical fertilizers, heat accumulating agents, ceramic binders, electric insulations for paper condensers and electric wires and cables, neutron decelerating agents, textile processing aids, water-repelling agents for building materials, protecting agents for coatings, calendering agents, thixotropy imparting agents, hardness imparting agents for the cores of pencils and crayons, substrates for carbon ink, electrophotographic toners, lubricants for molding of synthetic resins, mold mold releasing agents, resin coloring agents, hot-melt adhesives, and lubricating greases.

Novel random copolymers of the invention in which the mole ratio of the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to the polymerized unit from ethylene is from 3:97 to 20:80, preferably from 5:95 to 10:90 (measured by  $^{13}\text{C}$ -NMR analysis), and which have an intrinsic viscosity, measured in decalin at 135°C, of 0.3 to 20 dV/g, preferably 1.0 to 20 dV/g, especially preferably 2 to 15 dV/g, a crystallinity, determined by X-ray diffraction, of not more than 10%, preferably not more than 5%, a melting point, measured by a differential scanning calorimeter of not more than 128°C, preferably not more than 100°C, and a glass transition temperature by DMA of 25 to 100°C, preferably 30 to 80°C, have excellent shape memorizing property and antivibration property in addition to excellent transparency, heat resistance, chemical and solvent resistance, electrical properties, optical properties and moldability, and show leather properties. Accordingly, they are useful as shape memorizing polymers and antivibration material.

It should be understood that the term "cycloolefin" as used in the proviso in the present specification broadly includes not only cycloolefins in the ordinary sense of the word, but also styrene and styrene derivatives and unsaturated polycyclic hydrocarbon compounds. Specific examples of the cycloolefins include cyclobutene, cyclopentene, cyclohexene, 3,4-dimethylcyclopentene, 3-methylcyclohexene, 2-(2-methylbutyl)-1-cyclohexene, styrene, alpha-methylstyrene, norbornene, methylnorbornene, ethylnorbornene, isobutylnorbornene, 2,3,3a,7a-tetrahydro-4,7-methano-1H-indene and 3a,5,6,7a-tetrahydro-4,7-methano-1H-indene, for example cycloolefins having a norbornene ring, such as norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, and 5-isobutyl-2-norbornene.

In view of the properties of the final random copolymer, the use of the catalyst composed of a vanadium compound and an organoaluminum compound is preferred in this invention. If desired, however, the vanadium compound in the catalyst may be replaced by a titanium or zirconium compound.

The random copolymers of this invention may be molded by known methods. For example, they can be extrusion-molded, injection-molded, blow-molded, or rotationally molded by using, for example, a vent-type extruder, a twin-screw extruder, a conical twin-screw extruder, a Cokneader, a plasticator, a mixtruder, a twin conical screw extruder, a planetary screw extruder, a gear-type extruder or a screwless extruder. In the molding process, known additives such as heat stabilizers, light stabilizers, antistatic agents, slip agents, anti-blocking agents, antihaze agents, lubricants, inorganic and organic fillers, dyes and pigments may be used as required.

Phenolic or sulfur-type antioxidants may be cited as examples of such additives. The phenolic antioxidants include, for example, phenols such as 2,6-di-tert-butyl-p-cresol, stearyl (3,3,-dimethyl-4-hydroxybenzyl)thioglycolate, stearyl beta-(4-hydroxy-3,5-di-tert-butylphenol)propionate, distearyl 3,5-di-tert-butyl-4-hydroxybenzyl phosphate, 2,4,6-tris (3',5'-di-tert-butyl-4'-hydroxybenzylthio)-1,3,5-triazine, distearyl (4-hydroxy-3-methyl-5-tert-butylbenzyl)malonate, 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis[6-(1-methylcyclohexyl)p-cresol], bis[3,5-bis(4-hydroxy-3-tert-butylphenyl)butyric acid] glycol ester, 4,4'-butylidenebis(6-tert-butyl-m-cresol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butene, bis[2-tert-butyl-4-methyl-6-(2-hydroxy-3-tert-butyl-5-methylbenzyl)phenyl] terephthalate, 1,3,5-tris(2,6-di-methyl-3-hydroxy-4-tert-butyl)benzyl isocyanurate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]methane, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris[(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxyethyl] isocyanurate, 2-octylthio-4,6-di(4-hydroxy-3,5-di-tert-butyl)phenoxy-1,3,5-triazine and 4,4'-thiobis(6-tert-butyl-m-cresol); and polyhydric phenol/carbolic acid oligoesters such as carbolic acid oligoesters (for example, having a degree of polymerization of 2, 3, 4, 5, 6, 7, 8, 9, 10) of 4,4'-butylidenebis(2-tert-butyl-5-methylphenol).

Examples of the sulfur-type antioxidant include dialkyl thiodipropionates such as dialauryl, dimyristyl or distearyl thiodipropionate, and esters (such as pentaerythritol tetralaurylthiopropionate) formed between alkylthiopropionic acids such as butyl-, octyl-, lauryl- or stearylthiopropionic acid and polyhydric alcohols (such as glycerol, trimethylolthane, trimethylolpropane, pentaerythritol or tris-hydroxyethyl diisocyanurate).

## EP 0 582 355 B1

Phosphorous-containing compounds may also be incorporated. Examples include trioctyl phosphite, triauryl phosphite, tridecyl phosphite, octyldiphenyl phosphite, tris(2,4-di-tert-butylphenyl) phosphite, triphenyl phosphite, tris(butoxyethyl) phosphite, tris(nonylphenyl) phosphite, distearyl pentaerythritol diphosphite, tetra-(tridecyl)-1,1,3-tris(2-methyl-5-tert-butyl-4-hydroxyphenyl)butane diphosphite, tetra(C<sub>12</sub>-C<sub>15</sub> mixed alkyl)-4,4'-isopropylidenediphenyl diphosphite, tetra(tridecyl)-4,4'-butylidenebis(3-methyl-6-tert-butylphenol) diphosphite, tris(3,5-di-tert-butyl-4-hydroxyphenyl) phosphite, tris(mono-di-mixed nonylphenyl) phosphite, hydrogenated 4,4'-isopropylidene diphenol polyphosphite, bis(octylphenyl).bis[4,4'-butylidenebis(3-methyl-6-tert-butylphenol)].1,6-hexanediol diphosphite, phenyl-4,4'-isopropylidenediphenol-pentaerythritol diphosphite, bis-(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, tris[4,4'-isopropylidenebis(2-tert-butylphenol)] phosphite, phenyldiisodecyl phosphite, di(nonylphenyl)-pentaerythritol diphosphite, tris(1,3-di-stearoyloxyisopropyl) phosphite, 4,4'-isopropylidenebis(2-tert-butylphenol)-di(nonylphenyl) phosphite, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite.

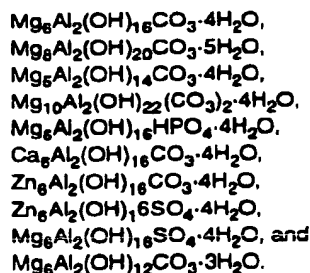
There can also be used 6-hydroxycoumarone derivatives such as alpha-, beta-, gamma- and delta-tocopherols and mixtures thereof, a 2,5-dimethyl-substitution product, 2,5,8-trimethyl-substituted product or 2,5,7,8-tetramethyl-substituted product of 2-(4-methyl-pent-3-enyl)-6-hydroxycoumarone, 2,2,7-trimethyl-5-tert-butyl-6-hydroxycoumarone, 2,2,5-trimethyl-7-tert-butyl-6-hydroxycoumarone, 2,2,5-trimethyl-6-tert-butyl-6-hydroxycoumarone, and 2,2-di-methyl-5-tert-butyl-6-hydroxycoumarone.

It is also possible to incorporate a compound represented by the general formula



wherein M represents Mg, Ca or Zn, A is an anion other than a hydroxyl anion, x, y and z are positive numbers, and a represents 0 or a positive number.

Examples of the compounds of the above formula are



There may also be added an antioxidant having a 2-benzofuranone skeleton, such as 3-phenyl-2-benzofuranone and 3-phenyl-4,6-di-tert-butyl-2-benzofuranone as disclosed in the specification of Japanese Laid-Open Patent Publication No. 501,181/1980.

Examples of the light stabilizers include hydroxybenzophenones such as 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone and 2,4-dihydroxybenzophenone; benzotriazoles such as 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and 2-(2'-hydroxy-3',5'-di-tert-amyphenyl)benzotriazole; benzoates such as phenyl salicylate, p-tert-butylphenyl salicylate, 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate; nickel compounds such as 2,2'-thiobis(4-tert-octylphenol) nickel salt, [2,2'-thiobis(4-tert-octylphenolate)]-n-butylamine nickel salt and (3,5-di-tert-butyl-4-hydroxybenzyl)phosphonic acid monoethyl ester nickel salt; substituted acrylonitriles such as methyl alpha-cyano-beta-methyl-beta-(p-methoxyphenyl)-acrylate; oxalic acid dianilides such as N'-2-ethylphenyl-N-ethoxy-5-tert-butylphenyl oxalic acid diamide and N-2-ethylphenyl-N'-2-ethoxyphenyl oxalic acid diamide; and hindered amine compounds such as bis(2,2,6,6-tetramethyl-4-piperidine)sebacate, poly[(6-(1,1,3,3-tetramethylbutyl)imino)-1,3,5-triazine-2,4-diyl 4-(2,2,6,6-tetramethylpiperidyl)imino]hexamethylene] and a condensation product of dimethyl succinate and 2-(4-hydroxy-2,2,6,6-tetramethyl-1-piperidyl)ethanol.

Examples of the lubricants include aliphatic hydrocarbons such as paraffin wax, polyethylene wax and polypropylene wax; higher fatty acids such as capric acid, lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachidic acid and behenic acid; metal salts of higher fatty acids such as lithium, calcium, sodium, magnesium and potassium salts of the above-exemplified fatty acids; aliphatic alcohols such as palmityl alcohol, cetyl alcohol and stearyl alcohol; aliphatic amides such as caproic amide, caprylic amide, capric amide, lauric amide, myristic amide, palmitic amide and stearic amide; esters formed between fatty acids and alcohols; and fluorine compounds such as fluoroalkylcarboxylic acids metal salts thereof, and metal salts of fluoroalkylsulfonic acids.



## EP 0 582 355 B1

Examples of the fillers include inorganic or organic fibrous fillers such as glass fibers, silver- or aluminum-coated glass fibers, stainless steel fibers, aluminum fibers, potassium titanate fibers, carbon fibers, whiskers, Kevlar® fibers and superhigh elastic polyethylene fibers; and inorganic or organic powdery, granular or flaky fillers such as talc, calcium carbonate, magnesium hydroxide, calcium oxide, magnesium sulfate, graphite, nickel powder, silver powder, copper powder, carbon black, silver-coated glass beads, aluminum-coated glass beads, aluminum flakes, stainless steel flakes and nickel-coated graphite.

The novel random copolymers of this invention may be used as a blend with various known polymers. Examples of such known polymers are shown below.

(A) Polymers derived from hydrocarbons having 1 or 2 unsaturated bonds

Polyolefins, such as polyethylene, polypropylene, polyisobutylene, poly(methylbutene-1), poly(4-methylpentene-1), poly(butene-1), polyisoprene, polybutadiene and polystyrene, or crosslinked products thereof.

Copolymers of the monomers constituting the above polymers with each other, such as ethylene/propylene copolymer, propylene/butene-1 copolymer, propylene/isobutylene copolymer, styrene/isobutylene copolymer, styrene/butadiene copolymer, terpolymers of ethylene, propylene and dienes such as hexadiene, bicyclopentadiene and 5-ethylidene-2-norbornene, and terpolymers of ethylene, butene-1 and dienes such as hexadiene, dicyclopentadiene and 5-ethylidene-2-norbornene.

Blends, grafted polymers, and block copolymers of these polymers may also be cited.

(B) Halogen-containing vinyl polymers

Polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polychloroprene, and chlorinated rubbers.

(C) Polymers derived from alpha,beta-unsaturated carboxylic acids or the derivatives thereof

Polyacrylate, polymethacrylate, polyacrylamide, and polyacrylonitrile.

Copolymers of the monomers constituting the above-exemplified polymers with other copolymerizable monomers, such as acrylonitrile/butadiene/styrene copolymer, acrylonitrile/styrene copolymer, and acrylonitrile/styrene/acrylate copolymer.

(D) Polymers derived from unsaturated alcohols, amines, acyl derivatives thereof, or acetals

Polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate and polyallyl melamine.

Copolymers of the monomers constituting the above-exemplified polymers with other copolymerizable monomers, such as ethylene/vinyl acetate copolymer.

(E) Polymers derived from epoxides

Polyethylene oxide and polymer derived from bisglycidyl ether.

(F) Polyacetals

Polyoxymethylene, polyoxyethylene, and polyoxymethylene containing ethylene oxide.

(G) Polyphenylene oxide

(H) polycarbonate

(I) Polysulfone

(J) Polyurethane and urea resins

(K) Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or aminocarboxylic acids or the corresponding lactams

Nylon 6, nylon 66, nylon 11, and nylon 12.

(L) Polyamide-polyethers

(M) Polyesters derived from dicarboxylic acids and dialcohols and/or hydroxycarboxylic acids or the corresponding lactones

Polyethylene terephthalate, polybutylene terephthalate and poly(1,4-dimethylolcyclohexane terephthalate).

(N) Crosslinked polymers derived from aldehydes and phenols, urea or melamine

Phenol/formaldehyde resin, urea/formaldehyde resin, and melamine/formaldehyde resin.

(O) Alkyd resins

Glycerin/phthalic acid resin.

(P) Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids and polyhydric alcohols using vinyl compounds as crosslinking agents, and halogen-containing modified resins thereof.

(Q) Natural polymers

Cellulose, rubber and protein, or derivatives thereof, such as cellulose acetate, cellulose propionate, cellulose acetate and cellulose ether.

When the copolymers of this invention are used as synthetic waxes, they may, of course, be mixed with various known waxes.

The random copolymers of this invention may be used as a blend with each other.

## EP 0 582 355 B1

The following Examples further illustrate the present invention in more detail.

## EXAMPLE 1

A thoroughly dried 3-liter separable flask was fitted with a stirring vane, a gas blowing inlet tube, a thermometer and a dropping funnel, and thoroughly purged with nitrogen.

One liter of toluene dehydrated and dried by molecular sieve was put into the flask.

While nitrogen was passed through the flask, 2 millimoles of dichloroethoxyoxovanadium and 30 g of 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (to be abbreviated DMON hereinafter) were introduced into the flask, and 20 millimoles of ethyl aluminum sesquichloride, into the dropping funnel.

A gaseous mixture of dry ethylene (40 liters/hr) and nitrogen (160 liters/hr) was passed through the flask kept at 10°C for 10 minutes through the gas blowing inlet tube.

The copolymerization reaction was started by adding ethyl aluminum sesquichloride from the dropping funnel, and carried out at 10°C for 30 minutes while passing the above gaseous mixture.

The solution during the copolymerization reaction was uniform and transparent, and no precipitation of the copolymer was observed.

Methanol (10 ml) was added to the polymer solution to stop the copolymerization reaction.

After the stopping of the reaction, the polymer solution was poured into a large amount of methanol to precipitate the resulting copolymer. The precipitate was washed with methanol and with acetone, dried in vacuo for one day at 60°C to obtain 35 g of the copolymer.

The copolymer had an ethylene content, measured by <sup>13</sup>C-NMR analysis, of 60 mole%, an intrinsic viscosity, measured in decalin at 135°C, of 1.9, and an iodine number of 1.0.

To measure its dynamical properties, the copolymer was molded into sheets having a thickness of 1 and 2 mm by a hot press at 230°C. X-ray diffraction analysis of these sheets shows that no scattering by crystals was observed, and the sheets had a crystallinity (W%) of 0%. Transparency was measured on the 1 mm-thick sheet by a haze meter in accordance with ASTM D1003-52, and found to be 10%. Flexural modulus and flexural yield strength were measured on the 2 mm-thick press sheet in accordance with ASTM D790, and were found to be  $2.2 \times 10^4$  kg/cm<sup>2</sup> and 730 kg/cm<sup>2</sup>, respectively. The glass transition temperature T<sub>g</sub> was found to be 130°C by measuring the loss modulus E'' at a temperature elevating rate of 5°C/min. by a Dynamic Mechanical Analyzer made by Du Pont, and determining T<sub>g</sub> from its peak temperature. To determine the melting point T<sub>m</sub>, the sample was heated at a rate of 10°C/min. in the range of -120 to 400°C by DSC (990 type made by Du Pont). The melting curve (peak) was not observed.

The dielectric constant and dielectric tangent (tan δ) of the sample, measured at 1 KHz by a dielectric loss measuring device made by Ando Electric Co., Ltd., were 1.9 and  $9.1 \times 10^{-6}$ , respectively.

To examine the chemical resistance of the sample, the press-formed sheet was immersed at room temperature in sulfuric acid (97%), aqueous ammonia (20%), acetone, and ethyl acetate for 20 hours, and then its appearance was observed. There was no change in color, reduction in transparency, deformation, dissolution, nor cracking.

Table 3 given below shows the heat decomposition temperature, dielectric constant and density of the co-polymer obtained in this example.

## EXAMPLES 2-10

The copolymerization reaction conditions were changed as shown in Table 1. Otherwise, the same operation as in Example 1 was performed. The conditions and the results are shown in Tables 1 to 3.

## EXAMPLES 11-12 AND COMPARATIVE EXAMPLE 1

Example 1 was repeated except that a 500 ml flask was used instead of the 3-liter flask, the amount of toluene was changed from 1 liter to 250 ml, and the flow rate of N<sub>2</sub> was changed from 160 liters/hr to 40 liters/hr. The results are shown in Tables 1 to 3.

## EP 0 582 355 B1

Table 1

Example	Catalyst		DMON (g)	Ethylene gas (L/hr)	Polymerization temperature (°C)	Amount of the copolymer yielded (g)
	VO(OEt)Cl <sub>2</sub> (mmoles)	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> (mmoles)				
1	2	20	30 <sup>1)</sup>	40	10	35
2	2	20	30 <sup>1)</sup>	20	10	28
3	2	20	30 <sup>1)</sup>	30	10	32
4	5	50	40	100	10	45
5	5	50	40	40	10	38
6	0.5	5	30	20	10	16
7	0.5	5	30	50	10	33
8	2	20	30 <sup>2)</sup>	40	10	32
9	2	20	30 <sup>3)</sup>	40	10	37
10	2	20	30 <sup>4)</sup>	40	10	36
11	0.125	1.25	2.5	40	20	7.0
12	0.125	1.25	2.2	40	20	8.5
Comp. Ex.1	0.125	1.25	1.3	45	30	6.0

1): 2-Methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene

2): 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene

3): 2-Ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene

4): 2-iso-Butyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene

EP 0 582 355 B1

Table 2

Example	$[\eta]$ 135°C dl/g	Ethylene content (mole%)	Iodine number	T <sub>g</sub> (DMA) (°C)	T <sub>m</sub> (DSC) (°C)	W <sup>C</sup> (X-rays) (%)	Haze (%)
1	1.9	60	1.0	130	-	0	10
2	1.4	43	0.5	168	-	0	7
3	1.6	55	0.8	141	-	0	8
4	1.5	70	0.7	105	-	0	11
5	1.0	49	0.4	150	-	0	8
6	2.5	53	0.6	144	-	0	8
7	3.2	69	0.8	113	-	0	11
8	1.7	58	0.5	131	-	0	8
9	1.0	63	0.8	128	-	0	7
10	1.9	65	1.0	127	-	0	7
11	2.7	94.1	0.7	38	85	4	15
12	3.2	92.2	0.7	43	60	5	10
Comp. Ex. 1	3.6	98.7	0.8	10	125	15	39

- to be continued -

## EP 0 582 355 B1

Table 2 (continued)

Example	Plexural modulus (kg/cm <sup>2</sup> )	Plexural yield strength (kg/cm <sup>2</sup> )	Dielectric tangent (tan δ)	Chemical resistance			
				97% sulfuric acid	20% aqueous ammonia	Acetone	Ethyl acetate
1	2.2x10 <sup>4</sup>	730	9.1x10 <sup>-5</sup>	○	○	○	○
2	2.7x10 <sup>4</sup>	980	9.8x10 <sup>-5</sup>	●	●	●	●
3	2.5x10 <sup>4</sup>	850	9.3x10 <sup>-5</sup>	●	●	●	●
4	1.4x10 <sup>4</sup>	450	8.6x10 <sup>-5</sup>	●	●	●	●
5	2.4x10 <sup>4</sup>	840	9.8x10 <sup>-5</sup>	●	●	●	●
6	2.2x10 <sup>4</sup>	1200	9.2x10 <sup>-5</sup>	●	●	●	●
7	1.3x10 <sup>4</sup>	930	9.0x10 <sup>-5</sup>	●	●	●	●
8	2.3x10 <sup>4</sup>	760	9.4x10 <sup>-5</sup>	●	●	●	●
9	2.1x10 <sup>4</sup>	720	9.6x10 <sup>-5</sup>	●	●	●	●
10	2.0x10 <sup>4</sup>	700	9.5x10 <sup>-5</sup>	●	●	●	●
11	0.3x10 <sup>4</sup>	230	1.5x10 <sup>-4</sup>	●	●	●	●
12	0.4x10 <sup>4</sup>	248	2.2x10 <sup>-4</sup>	●	●	●	●
Comp. Ex. 1	0.02x10 <sup>4</sup>	55	2.8x10 <sup>-4</sup>	●	●	●	●

Table 3

Example	Heat decomposition temperature by TGA(°C)	Dielectric constant (1 KHz)	Density (g/cm <sup>3</sup> )
1	380	1.9	1.021
2	377	2.0	1.027
3	390	2.1	1.024

Continuation of the Table on the next page

## EP 0 582 355 B1

Table 3 (continued)

Example	Heat decomposition temperature by TGA(°C)	Dielectric constant (1 KHz)	Density (g/cm <sup>3</sup> )
4	385	1.9	1.015
5	383	2.2	1.025
6	384	2.3	1.023
7	390	1.9	1.016
8	381	1.0	1.021
9	382	2.0	1.019
10	374	2.1	1.018
11	385	2.3	0.958
12	380	2.4	0.962
Comp. Ex. 1	375	2.5	0.930

## EXAMPLES 13-17

The copolymerization reaction conditions were changed as shown in Table 4, and otherwise the same operation as in Example 1 was performed. The results are shown in Tables 5-1, 5-2 and 5-3.

Table 4

Example	Catalyst		DMON (g)	Ethylene gas (L/hr)	Polymerization temperature (°C)	Amount of the copolymer yielded (g)
	VO(OEt)Cl <sub>2</sub> (mmoles)	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> (mmoles)				
13	1	10	30 <sup>a)</sup>	28	10	12.4
14	1	10	30 <sup>a)</sup>	40	10	24.0
15	1	10	30 <sup>a)</sup>	80	10	28.0
16	1	10	30 <sup>b)</sup>	35	10	23.1
17	1	10	30 <sup>b)</sup>	55	10	26.2

a): 2,3-Dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene

b): 2,3-Diethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene

EP 0 582 355 B1

Table 5-1

Example	[ $\eta$ ] 135°C (dl/g)	Ethylene content (mole%)	Iodine number	T <sub>g</sub> (PMA) (°C)	T <sub>m</sub> (DSC) (°C)	W <sup>C</sup> (X-rays) (%)	Base (%)
13	1.13	57	0.6	148	-	0	5
14	1.60	69	0.8	118	-	•	9
15	2.11	74	0.7	106	-	•	9
16	1.68	64	0.7	134	-	•	7
17	1.94	72	0.9	110	-	•	10

Table 5-2

Example	Plexural modulus (kg/cm <sup>2</sup> )	Plexural yield strength (kg/cm <sup>2</sup> )	Dielectric tangent (tan $\delta$ )	Chemical resistance			
				97% sulfuric acid	20% aqueous ammonia	Acetone	Ethyl acetate
13	$2.4 \times 10^4$	810	$9.8 \times 10^{-5}$	○	○	○	○
14	$1.9 \times 10^4$	650	$1.1 \times 10^{-4}$	•	•	•	•
15	$1.6 \times 10^4$	580	$1.1 \times 10^{-4}$	•	•	•	•
16	$2.1 \times 10^4$	750	$1.2 \times 10^{-4}$	•	•	•	•
17	$1.8 \times 10^4$	600	$1.0 \times 10^{-4}$	•	•	•	•

Table 5-3

Example	Heat decomposition temperature by TGA (°C)	Dielectric constant (1 KHz)	Density (g/cm <sup>3</sup> )
13	385	1.9	1.022
14	380	2.1	1.018

Continuation of the Table on the next page

## EP 0 582 355 B1

Table 5-3 (continued)

Example	Heat decomposition temperature by TGA (°C)	Dielectric constant (1 KHz)	Density (g/cm <sup>3</sup> )
15	373	2.2	1.014
16	376	2.0	1.021
17	377	2.2	1.018

## EXAMPLE 18

A thoroughly dried 500 ml separable flask was fitted with a stirring vane, a gas blowing inlet tube, a thermometer and a dropping funnel, and thoroughly purged with nitrogen.

Toluene (250 ml) dehydrated and dried by molecular sieve was put into the flask.

While nitrogen was passed through the flask, 7.5 g of the compound (g) in Table 6, and 2.5 millimoles of ethyl aluminum sesquichloride were introduced into the flask, and 0.25 millimole of dichloroethoxyoxovanadium was added to the dropping funnel. A gaseous mixture composed of dry ethylene (10 liters/hr) and nitrogen (40 liters/hr) was passed into the flask kept at 10°C for 10 minutes through the gas blowing inlet tube. From the dropping funnel, dichloroethoxyoxovanadium was added to start the copolymerization. While passing the gaseous mixture, the copolymerization was carried out at 10°C for 30 minutes. During the copolymerization, the solution was uniform and transparent, and no precipitation of the copolymer was observed. Methanol (5 ml) was added to the polymer solution to stop the copolymerization reaction. The polymer solution after the stopping of the reaction was poured into large amounts of methanol and acetone to precipitate the copolymer. The precipitate was further washed with methanol and acetone, and dried in vacuo for one day at 60°C to obtain 5.3 g of the copolymer. The copolymer had an ethylene content, measured by <sup>13</sup>C-NMR analysis, of 59 mole%, an intrinsic viscosity, measured in decalin at 135°C, of 1.4 dl/g, and an iodine number of 0.9. To measure its dynamical properties, the copolymer was molded into sheets having a thickness of 1 and 2 mm by a hot press at 230°C. X-ray diffraction analysis of these sheets shows that no scattering by crystals was observed, and the sheets had a crystallinity (WC) of 0%. Transparency was measured on the 1 mm-thick sheet by a haze meter in accordance with ASTM D1003-52, and found to be 9%. Flexural modulus and flexural yield strength were measured on the 2 mm-thick press sheet in accordance with ASTM D790, and were found to be  $2.5 \times 10^4$  kg/cm<sup>2</sup> and 810 kg/cm<sup>2</sup>, respectively. The glass transition temperature T<sub>g</sub> was found to be 150°C by measuring the loss modulus E'' at a temperature elevating rate of 5°C/min. by a dynamic mechanical analyzer (DMA) made by Du Pont, and determining T<sub>g</sub> from its peak temperature. To determine the melting point T<sub>m</sub>, the sample was heated at a rate of 10°C/min. in the range of -120 to 400°C by DSC (990 type made by Du Pont). The melting curve (peak) was not observed.

The electrical properties of the copolymer were measured at 1 KHz by a dielectric loss measuring device made by Ando Electric Co., Ltd. It was found to have a dielectric constant of 1.9 and a dielectric tangent (tan δ) of  $2.3 \times 10^{-4}$ .

To examine the chemical resistance of the copolymer, the press-formed sheet was immersed at room temperature in sulfuric acid (97%), aqueous ammonia (20%), acetone, and ethyl acetate for 20 hours, and then its appearance was observed. There was no change in color, reduction in transparency, deformation, dissolution, nor cracking.

The copolymer also had a density, determined by the density gradient tube method, of 1.032 g/cm<sup>3</sup>, a refractive index (n<sub>D</sub>), measured by an Abbe refractometer, of 1.540, and a pencil hardness, as a measure of hardness, of H.

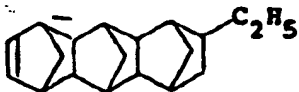

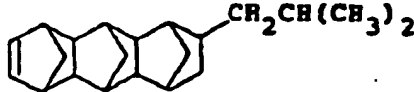
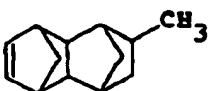

## EXAMPLES 19-30

The same operation as in Example 18 was carried out except that the monomers were changed as indicated in Table 6, and the copolymerization conditions were changed as shown in Table 7. The results are shown in Tables 8 and 9. Tables 7, 8 and 9 also show the conditions and the results used and obtained in Example 18.



EP 0 582 355 B1

Table 6

Designation	Compound	
g		12-Ethyl-hexacyclo- [6,6,1,1 <sup>3</sup> ,6,1 <sup>10</sup> ,13,0 <sup>2</sup> ,7,- 0 <sup>9</sup> ,14]heptadecene-4
h		12-Methyl-hexacyclo- [6,6,1,1 <sup>3</sup> ,6,1 <sup>10</sup> ,13,0 <sup>2</sup> ,7,- 0 <sup>9</sup> ,14]heptadecene-4
i		12-iso-Butyl-hexacyclo- [6,6,1,1 <sup>3</sup> ,6,1 <sup>10</sup> ,13,0 <sup>2</sup> ,7,- 0 <sup>9</sup> ,14]heptadecene-4
j		9-Methyl-tetracyclo- [4,4,0,1 <sup>2</sup> ,5,1 <sup>7</sup> ,10]- dodecene-3
k		Hexacyclo[6,6,1,1,1,0,0]- heptadecene-4

EP 0 582 355 B1

Table 7

Example	Catalyst		Amounts of monomers fed			Polymeri- zation tempera- ture (°C)	Amount of the copolymer yielded (g)
	VO(OC <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> (mmoles)	Al(C <sub>2</sub> H <sub>5</sub> ) <sub>1.5</sub> Cl <sub>1.5</sub> (mmoles)	Ethylene (l/hr)	Polycyclic monomer (g)			
18	0.25	2.5	20	g	7.5	10	5.3
19	"	"	30	g	"	"	6.3
20	"	"	10	g	"	"	4.2
21	"	"	20	h	"	"	5.2
22	"	"	30	h	"	"	6.0
23	"	"	20	i	"	"	4.9
24	"	"	30	i	"	"	5.7
25	"	"	10	g/j	5.0/2.5	"	3.9
26	"	"	20	g/j	"	"	5.7
27	"	"	10	k	7.5	"	3.6
28	"	"	20	k	"	"	4.8
29	"	"	30	k	"	"	5.9
30 (*)	3.0	30	90	k	20	30	3.2

(\*): Instead of N<sub>2</sub>, H<sub>2</sub> was passed at 150 liters/hr.

## EP 0 582 355 B1

Table 8

Example	$[\eta]$ (dl/g)	Ethylene content (mole%)	Iodine number	T <sub>g</sub> (DMA) (°C)	T <sub>m</sub> (DSC) (°C)	W <sup>c</sup> (X-rays) (%)	Heat decom- position tempera- ture by TGA (°C)	Density (g/cm <sup>3</sup> )
18	1.4	59	0.9	150	-	0	383	1.032
19	1.6	65	1.0	134	-	0	388	1.030
20	1.1	49	0.7	173	-	0	385	1.033
21	1.2	57	0.7	153	-	0	384	1.033
22	1.6	67	1.0	133	-	0	380	1.025
23	1.3	60	0.9	148	-	0	381	1.031
24	1.6	68	0.8	130	-	0	382	1.025
25 (*1)	1.4	47	0.9	170	-	0	388	1.035
26 (*2)	2.0	58	1.1	151	-	0	385	1.028
27	1.2	48	1.0	171	-	0	389	1.033
28	1.5	57	0.9	156	-	0	385	1.029
29	1.8	64	0.8	138	-	0	383	1.026
30	0.08	58	0.9	140(*3)	-	0	379	1.030

(\*1) ; 9-Methyl-tetracyclo[4,4,0,12,5,17,10]dodecene-3 (10 moles)

(\*2) ; 9-Methyl-tetracyclo[4,4,0,12,5,17,10]dodecene-3 (13 moles)

(\*3) Softening point

## EP 0 582 355 B1

Table 9

Ex- ample	Refrac- tive index ( $n_D$ )	Dielectric constant at 1 KHz	Dielectric tangent at 1 KHz ( $\times 10^{-4}$ )	Flexural modulus ( $\text{kg/cm}^2$ $\times 10^{-4}$ )	Flexural yield strength ( $\text{kg/cm}^2$ )	Pencil hard- ness	Haze (%)	Chemical resistance			
								97% sulfuric acid	20% aqueous ammonia	Acetone	Ethyl acetate
18	1.540	1.9	2.3	2.5	810	H	9	O	O	O	O
19	1.539	1.9	2.1	2.3	930	H	8	"	"	"	"
20	1.544	2.0	2.6	2.9	1050	2H	10	"	"	"	"
21	1.541	2.1	2.8	2.6	860	H	6	"	"	"	"
22	1.536	2.2	3.1	2.1	850	HB	8	"	"	"	"
23	1.544	2.4	3.2	2.6	890	H	7	"	"	"	"
24	1.534	2.3	3.2	2.1	800	HB	6	"	"	"	"
25	1.544	2.3	3.1	2.8	950	2H	7	"	"	"	"
26	1.540	2.4	3.3	2.6	850	H	8	"	"	"	"
27	1.543	2.5	3.4	2.8	1100	2H	8	"	"	"	"
28	1.540	2.3	2.5	2.5	780	H	8	"	"	"	"
29	1.539	2.3	2.7	2.2	870	HB	7	"	"	"	"
30	1.541	2.4	2.5	-	-	2B	9	"	"	"	"

## EP 0 582 355 B1

## EXAMPLE 31

A thoroughly dried 500 ml separable flask was fitted with a stirring vane, a gas blowing inlet tube, a thermometer and a dropping funnel, and thoroughly purged with nitrogen.

Toluene (250 ml) dehydrated and dried by molecular sieve was put into the flask.

While nitrogen was passed through the flask, 7.5 g of pentacyclo[6,5,1,1<sup>3,8</sup>,0<sup>2,7</sup>,0<sup>9,13</sup>]pentadecene-4 and 2.5 millimoles of ethyl aluminum sesquichloride were introduced into the flask, and 0.25 millimole of dichloroethoxyoxovanadium was added to the dropping funnel.

A gaseous mixture composed of dry ethylene (20 liters/hr) and nitrogen (40 liters/hr) was passed into the flask kept at 10°C for 10 minutes through the gas blowing inlet tube.

From the dropping funnel, dichloroethoxyoxovanadium was added to start the copolymerization. While passing the gaseous mixture, the copolymerization was carried out at 10°C for 30 minutes.

During the copolymerization, the solution was uniform and transparent, and no precipitation of the copolymer was observed.

Methanol (3 ml) was added to the polymer solution to stop the copolymerization reaction.

The polymer solution after the stopping of the reaction was poured into large amounts of methanol and acetone to precipitate the copolymer. The precipitate was further washed with methanol and acetone, and dried in vacuo for one day at 60°C to obtain 7.2 g of the copolymer.

The copolymer had an ethylene content, measured by <sup>13</sup>C-NMR analysis, of 55 mole%, an intrinsic viscosity, measured in decalin at 135°C, of 2.1 dl/g, and an iodine number of 0.7.

To measure its dynamical properties, the copolymer was molded into sheets having a thickness of 1 and 2 mm by a hot press at 230°C. X-ray diffraction analysis of these sheets shows that no scattering by crystals was observed, and the sheets had a crystallinity (WC) of 0%. Transparency was measured on the 1 mm-thick sheet by a haze meter in accordance with ASTM D1003-52, and found to be 8%. Flexural modulus and flexural yield strength were measured on the 2 mm-thick press sheet in accordance with ASTM D790, and were found to be 2.5 x 10<sup>4</sup> kg/cm<sup>2</sup> and 850 kg/cm<sup>2</sup>, respectively. The glass transition temperature T<sub>g</sub> was found to be 149°C by measuring the loss modulus E'' at a temperature elevating rate of 5°C/min. by a Dynamic Mechanical Analyzer made by Du Pont, and determining T<sub>g</sub> from its peak temperature. To determine the melting point T<sub>m</sub>, the sample was heated at a rate of 10°C/min. in the range of -120 to 400°C by DSC (990 type made by Du Pont). The melting curve (peak) was not observed.

The electrical properties of the copolymer were measured at 1 KHz by a dielectric loss measuring device made by Ando Electric Co., Ltd. It was found to have a dielectric constant of 2.0 and a dielectric tangent (tan δ) of 2.8 x 10<sup>-4</sup>.

To examine the chemical resistance of the press-formed sheet, it was immersed at room temperature in sulfuric acid (97%), aqueous ammonia (20%), acetone, and ethyl acetate for 20 hours, and then its appearance was observed. There was no change in color, reduction in transparency, deformation, dissolution, nor cracking.


The copolymer also had a heat decomposition temperature (the weight loss initiation temperature), determined by a thermobalance, of 390°C, a density, determined at 23°C by the density gradient method, of 1.025 g/cm<sup>3</sup>, a refractive index (n<sub>D</sub>), measured by an Abbe refractometer, of 1.536, and a pencil hardness, as a measure of surface hardness, of H.

## EXAMPLES 32-36

The same operation as in Example 31 was carried out except that the monomer components were changed as shown in Table 10, and the copolymerization conditions were changed as shown in Table 10. The results are shown in Tables 10, 11 and 12.

EP 0 582 355 B1

Table 10

Example	Catalyst		Amounts of monomers fed		Polymeri- zation tempera- ture (°C)	Amount of the copolymer yielded (g)
	VO(OC <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> (mmoles)	Al(C <sub>2</sub> H <sub>5</sub> ) <sub>1.5</sub> Cl <sub>1.5</sub> (mmoles)	Ethylene (g/hr)	Polycyclic monomer  (g)		
31	0.25	2.5	20	7.5	10	6.5
32	"	"	8	"	"	5.2
33	"	"	30	"	"	7.0
34	"	"	40	"	"	7.8
35 (*1)	2.5	25	80	15	30	3.8
36 (*2)	2.5	"	80	"	"	3.7

(\*1): Instead of N<sub>2</sub>, H<sub>2</sub> was passed at 80 liters/hr.(\*2): Instead of N<sub>2</sub>, H<sub>2</sub> was passed at 200 liters/hr.

## EP 0 582 355 B1

Table II

Example	[ $\eta$ ] (dl/g)	Ethylene content (mole%)	Iodine number	T <sub>g</sub> (DMA) (°C)	Softening temperature (TMA) (°C)	T <sub>m</sub> (DSC) (°C)	w <sup>C</sup> (X-rays) (%)	Heat decom- position tempera- ture by TGA (°C)	Density (g/cm <sup>3</sup> )
31	2.1	55	0.7	149	-	-	0	390	1.025
32	1.7	45	0.5	171	-	-	0	394	1.026
33	2.3	63	1.0	128	-	-	0	395	1.024
34	3.0	72	0.8	100	-	-	0	383	1.020
35	0.10	59	0.9	-	128	-	0	370	1.021
36	0.07	57	0.8	-	129	-	0	372	1.021

## EP 0 582 355 B1

Table 12

Ex- ample	Reflac- tive index ( $n_D$ )	Dielectric constant at 1 KHz	Dielectric tangent at 1 KHz ( $\times 10^{-4}$ )	Flexural modulus ( $\text{kg/cm}^2$ $\times 10^{-4}$ )	Flexural yield strength ( $\text{kg/cm}^2$ )	Pencil hard- ness	Chemical resistance			
							97% sulfuric acid	20% aqueous ammonia	Acetone	Ethyl acetate
31	1.536	2.0	2.8	2.5	850	HB	○	○	○	○
32	1.539	1.9	2.5	2.7	1010	H	"	"	"	"
33	1.534	2.1	2.9	2.2	880	HB	"	"	"	"
34	1.530	2.2	3.0	1.9	680	B	"	"	"	"
35	1.534	2.3	3.0	-	-	2B	"	"	"	"
36	1.543	2.2	3.5	-	-	2B	"	"	"	"

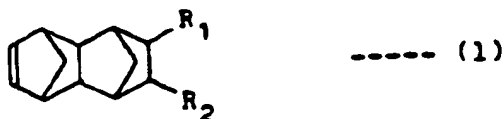


## EP 0 582 355 B1

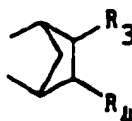
## Claims

1. A transparent random copolymer characterized in that

(A) said copolymer comprises polymerized units derived from ethylene and polymerized units derived from a 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the following formula (1)



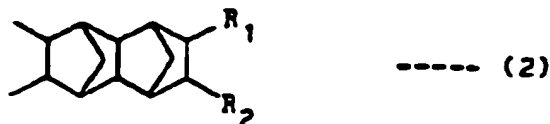
wherein  $R_1$  and  $R_2$  are identical or different and each represents a hydrogen atom, a halogen atom or an alkyl group, or  $R_1$  and  $R_2$  may be bonded to each other to form a trimethylene group or a group represented by the following formula



in which  $R_3$  and  $R_4$  are identical or different and each represents a hydrogen atom, a halogen atom or an alkyl group.

(B) the mole ratio of polymerized units derived from 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to polymerized units derived from ethylene is from 3:97 to 95:5,

(C) the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is incorporated in the polymer chain as polymerized units represented by the following formula (2)



wherein  $R_1$  and  $R_2$  are as defined above, and

(D) said copolymer has a glass transition temperature, measured by a dynamic mechanical analyzer, of at least 25°C, subject to the proviso that said copolymer does not consist essentially of said at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the formula (1), ethylene and at least one alpha-olefin of at least 3 carbon atoms and/or cycloolefin, wherein the mole ratio of polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to polymerized units from ethylene is from 3:97 to 95:5, and the mole ratio of polymerized units from the at least one alpha-olefin and/or cycloolefin to the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is from 95:5 to 20:80.

2. A transparent random copolymer according to claim 1 which has an intrinsic viscosity, measured in decalin at 135°C, of 0.005 to 20 dl/g.
3. A transparent random copolymer according to claim 1 or 2 wherein, in formula (1), at least one of  $R_1$  and  $R_2$  is an alkyl group.
4. A transparent random copolymer according to claim 1, 2 or 3 which has a glass transition temperature of 30 to 220°C.
5. A process for producing a transparent random copolymer as claimed in any one of the preceding claims which comprises copolymerizing a monomer mixture comprising ethylene and at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of the formula (1) in a hydrocarbon medium under a pressure of up to 4.9 MPa (0 to 50 kg/cm<sup>2</sup>) in the presence of a catalyst formed from a vanadium compound and an organoaluminum compound which are soluble in the hydrocarbon medium.
6. Shaped articles of a transparent random copolymer as claimed in any one of claims 1 to 4.

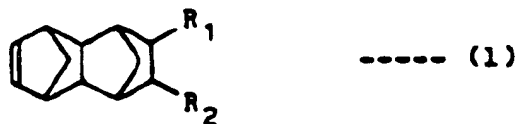
## EP 0 582 355 B1

7. A transparent random copolymer as defined in claim 1 which is obtainable by copolymerizing a monomer mixture comprising ethylene and at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of the formula (1) in a hydrocarbon medium under a pressure at 0 to 4.9 Mpa (0 to 50 kg/cm<sup>2</sup>) in the presence of a catalyst formed from a vanadium compound and an organoaluminum compound which are soluble in the hydrocarbon medium.

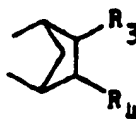
## Patentansprüche

1. Transparentes statistisches Copolymer, dadurch gekennzeichnet, daß

(A) das Copolymer umfaßt polymerisierte Einheiten, abgeleitet von Ethylen, und polymerisierte Einheiten, abgeleitet von 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, angegeben durch die Formel (1)



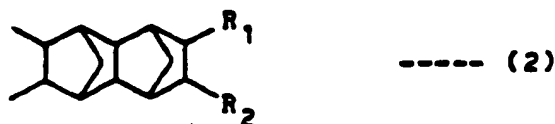
in der R<sub>1</sub> und R<sub>2</sub> gleich oder verschieden sind und jeweils ein Wasserstoffatom, ein Halogenatom oder eine Alkylgruppe bedeuten, oder R<sub>1</sub> und R<sub>2</sub> miteinander verbunden sein können unter Bildung einer Trimethylen-gruppe oder einer Gruppe, angegeben durch die Formel



wobei R<sub>3</sub> und R<sub>4</sub> gleich oder verschieden sind und jeweils ein Wasserstoffatom, ein Halogenatom oder eine Alkylgruppe bedeuten,

(B) das Molverhältnis von polymerisierten Einheiten, abgeleitet von dem 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, zu polymerisierten Einheiten, abgeleitet von Ethylen, 3:97 bis 95:5 beträgt,

(C) das 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin in der Polymerkette eingebaut ist in Form von polymerisierten Einheiten, angegeben durch die Formel (2)



wobei R<sub>1</sub> und R<sub>2</sub> wie oben definiert sind, und

(D) das Copolymer eine Glasübergangstemperatur, gemessen mit Hilfe eines dynamisch-mechanischen Analysators, von mindestens 25°C besitzt mit der Maßgabe, daß das Copolymer nicht im wesentlichen aus dem einen 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, angegeben durch die Formel (1), Ethylen und mindestens einem α-Olefin mit mindestens 3 Kohlenstoffatomen und/oder Cycloolefin besteht, wobei das Molverhältnis von polymerisierten Einheiten, abgeleitet von mindestens einem α-Olefin und/oder Cycloolefin, zu polymerisierten Einheiten, abgeleitet von dem 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, 95:5 bis 20:80 beträgt.

2. Transparentes statistisches Copolymer nach Anspruch 1 mit einer Grundviskosität, gemessen in Decalin bei 135°C, von 0,005 bis 20 dl/g.
3. Transparentes statistisches Copolymer nach Anspruch 1 oder 2, wobei in Formel (1) mindestens einer der Reste R<sub>1</sub> und R<sub>2</sub> eine Alkylgruppe ist.
4. Transparentes statistisches Copolymer nach Anspruch 1, 2 oder 3, das eine Glasübergangstemperatur von 30 bis

## EP 0 582 355 B1

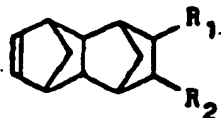
220°C besitzt.

5. Verfahren zur Herstellung eines transparenten statistischen Copolymers nach einem der vorangehenden Ansprüche, umfassend das Copolymerisieren eines Monomergemisches, umfassend Ethylen und mindestens ein 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin der Formel (1), in einem Kohlenwasserstoffmedium unter einem Druck von bis zu 4,9 MPa (0 bis 50 kg/cm<sup>2</sup>) in Gegenwart eines Katalysators, gebildet aus einer Vanadiumverbindung und einer Organoaluminiumverbindung, die in dem Kohlenwasserstoffmedium löslich sind.
6. Formkörper aus einem transparenten statistischen Copolymer nach einem der Ansprüche 1 bis 4.
7. Transparentes statistisches Copolymer nach Anspruch 1, das erhältlich ist durch Copolymerisieren eines Monomergemisches, umfassend Ethylen und mindestens ein 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin der Formel (1), in einem Kohlenwasserstoffmedium unter einem Druck von bis zu 4,9 MPa (0 bis 50 kg/cm<sup>2</sup>) in Gegenwart eines Katalysators, gebildet aus einer Vanadiumverbindung und einer Organoaluminiumverbindung, die in dem Kohlenwasserstoffmedium löslich sind.

## Revendications

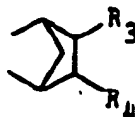
1. Copolymère statistique transparent caractérisé en ce que

(A) ledit copolymère comprend des motifs polymérisés dérivés de l'éthylène et des motifs polymérisés dérivés d'un 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène représenté par la formule suivante (1) :



(1)

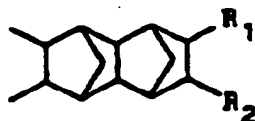
dans laquelle R<sub>1</sub> et R<sub>2</sub> sont identiques ou différents, et chacun représente un atome d'hydrogène, un atome d'halogène ou un groupe alkyle, ou R<sub>1</sub> et R<sub>2</sub> peuvent être reliés l'un à l'autre pour former un groupe triméthylène ou un groupe représenté par la formule suivante :



dans laquelle R<sub>3</sub> et R<sub>4</sub> sont identiques ou différents, et chacun représente un atome d'hydrogène, un atome d'halogène, ou un groupe alkyle,

(B) le rapport molaire des motifs polymérisés dérivés de 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène aux motifs polymérisés dérivés de l'éthylène vaut de 3:97 à 95:5,

(C) on incorpore le 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène dans la chaîne du polymère comme motifs polymérisés représentés par la formule suivante (2)



(2)

dans laquelle R<sub>1</sub> et R<sub>2</sub> ont les définitions indiquées précédemment, et

(D) ledit copolymère a une température de transition vitreuse, mesurée par un analyseur mécanique dynamique, valant au moins 25°C, à condition que ledit copolymère ne consiste pas essentiellement en au moins l'un de ces 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène représenté par la formule (1), éthylène, et en au moins une alpha-oléfine comportant au moins trois atomes de carbone et/ou cyclooléfine, dans lequel le rapport molaire des motifs polymérisés du 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène aux motifs polymérisés de l'éthylène vaut de 3:97 à 95:5, et le rapport molaire des motifs polymérisés dérivés d'au moins une alpha-oléfine et/ou cyclooléfine aux motifs polymérisés dérivés du 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène vaut de 95:5 à 20:80.

## EP 0 582 355 B1

2. Copolymère statistique transparent conforme à la revendication 1, qui a une viscosité intrinsèque, mesurée dans la décaline à 135°C, d'au moins 0,005 à 20 dl/g.
3. Copolymère statistique transparent conforme à la revendication 1 ou 2, dans lequel dans la formule (1), au moins l'un des  $R_1$  et  $R_2$  représente un groupe alkyle.
4. Copolymère statistique transparent conforme à la revendication 1, 2, ou 3, qui a une température de transition vitreuse de 30 à 220°C.
5. Procédé de préparation d'un copolymère statistique transparent conforme à l'une quelconque des précédentes revendications, qui comprend la copolymérisation d'un mélange de monomères contenant l'éthylène et au moins un 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène de formule (1) dans un milieu d'hydrocarbures sous une pression ne dépassant pas 4,9 MPa (0 à 50 kg/cm<sup>2</sup>), en la présence d'un catalyseur formé à partir d'un composé de vanadium et d'un composé organique d'aluminium qui sont solubles dans le milieu d'hydrocarbures.
6. Articles façonnés avec un copolymère statistique transparent conforme à l'une quelconque des revendications 1 à 4.
7. Copolymère statistique transparent conforme à la revendication 1, qui peut être obtenu par copolymérisation d'un mélange de monomères contenant l'éthylène et au moins un 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydronaphtalène de formule (1) dans un milieu d'hydrocarbures sous une pression de 0 à 4,9 MPa (0 à 50 kg/cm<sup>2</sup>) en la présence d'un catalyseur formé à partir d'un composé de vanadium et d'un composé organique d'aluminium qui sont solubles dans le milieu d'hydrocarbures.